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Supporting Information

Oxidant Controlled Pd-Catalyzed Selective Oxidation of Primary Alcohols

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General information

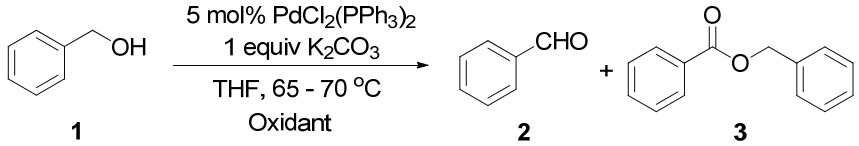
All reactions were isolated from moisture and oxygen by a nitrogen atmosphere with a balloon fitted on a Schlenk tube. All glassware was oven dried at 110 ^{o}C for hours and cooled down under vacuum. THF was purified by distillation with sodium. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. $PdCl_2(PPh_3)_2$,[1] $PdCl_2(dppf)$[2] and desyl chloride[3] were synthesized according to literature procedure. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 ^{o}C). Gas chromatographic analyses were performed on Varian GC 2000 gas chromatography instrument with a FID detector and biphenyl was added as the internal standard. GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. ^{1}H and ^{13}C NMR data were recorded with Varian Mercury (300 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and *d*-solvent peaks (77.00 ppm, chloroform), respectively.

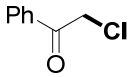
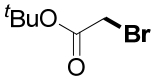
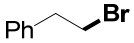
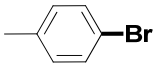
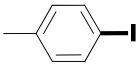
General procedure

General procedure for the selective and general Pd-catalyzed oxidative esterification of primary alcohol with benzyl chloride as the oxidant: $PdCl_2(PPh_3)_2$ (17.5 mg, 0.025 mmol) and K_2CO_3 (69.5 mg, 0.50 mmol) were placed in a Shlenck tube, which was filled with nitrogen by using standard Schlenk techniques. THF (2.0 mL), benzyl chloride (63.3 mg, 0.50 mmol) and alcohol **1** (0.50 mmol) were consequently added to the reaction tube. The reaction mixture was stirred at 65 - 70 ^{o}C for 20 h. Then the suspension solution was extracted by ethyl acetate (3 x 5 mL), and the resulting mixture was quenched with water. The organic layers were combined, and dried over sodium sulfate. The pure product was obtained by flash column chromatography on silica gel (petroleum : ethyl acetate = 50:1).

General procedure for Pd-catalyzed oxidation of primary alcohol with desyl chloride as the oxidant: $PdCl_2(PPh_3)_2$ (17.5 mg, 0.025 mmol), desyl chloride (230.7mg, 0.50 mmol) and K_2CO_3 (69.5 mg, 0.50 mmol) were placed in a Shlenck tube, which was filled with nitrogen by using standard Schlenk techniques. THF and alcohol **1** (0.50 mmol) were consequently added to the reaction tube. The reaction systems were stirred at 65 - 70 ^{o}C for 20 h. The resulting mixture was quenched with water. The yield was then determined by GC analysis with biphenyl as the internal standard.

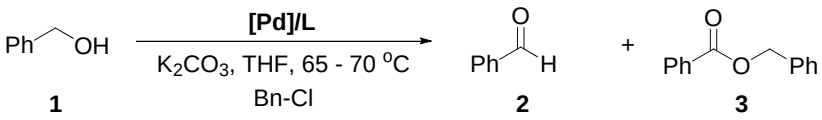
Table 1S. Oxidant effect for the palladium catalyzed oxidation of benzyl alcohol



Entry	Oxidant	Yield (%)[a]	
		2	**3**
1		5	74
2		91	n.d.
3		60	n.d.
4		< 5	n.d.
5		73	10
6		49	n.d.
7	O_2	43	n.d.

[a] Determined by GC analysis

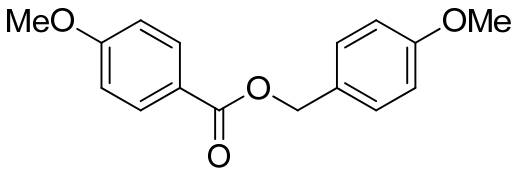
Table 2S. Ligand dissociation effect for the oxidative esterification of benzyl alcohol with benzyl chloride as the oxidant



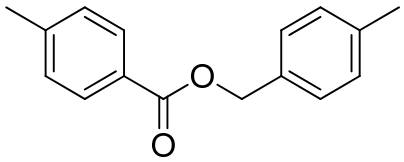
Entry	[Pd]	L	Yield (%)[a]	
			2	**3**
1	$PdCl_2(PPh_3)_2$	—	n.d.	96
2	$PdCl_2$(dppf)	—	27	14

[a] Determined by GC analysis

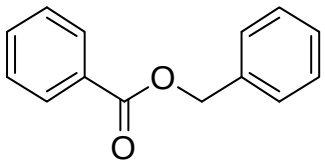
Detail descriptions for products



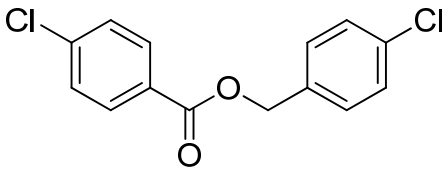
4-Methoxybenzyl 4-methoxybenzoate (3a)[4]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.34 (s, *J* = 8.4 Hz, 2H), 6.78 – 6.92 (m, 4H), 5.23 (s, 2H), 3.60 – 3.85 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.09, 163.20, 159.41, 131.53, 129.87, 128.23, 122.47, 113.75, 113.41, 66.08, 55.22, 55.08.



4-Methylbenzyl 4-methylbenzoate (3b)[5]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.24 – 7.16 (m, 4H), 5.29 (s, 2H), 2.39 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.79, 143.88, 138.25, 133.41, 139.97, 129.48, 129.28, 128.57, 127.69, 66.72, 21.89, 21,49.

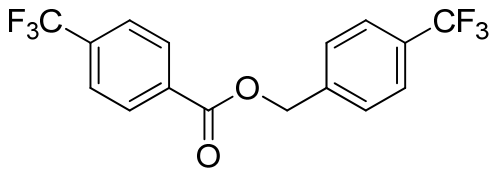


Benzyl benzoate (3c)[6]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.4 Hz, 2H), 7.51 –7.42 (m, 1H), 7.40 – 7.20 (m, 7H), 5.27 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.35, 136.00, 132.96, 130.07, 129.64, 128.53, 128.31, 128.17, 128.10, 66.62.

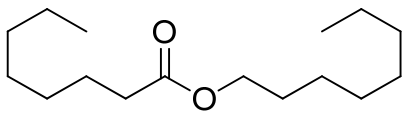


4-Chlorobenzyl 4-chlorobenzoate (3d)[7]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.28 – 7.25 (m, 4H), 5.22 (s, 2H); ^{13}C NMR (75

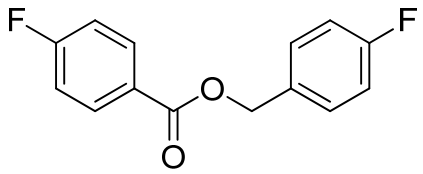
MHz, $CDCl_3$) δ 165.39, 139.60, 134.24, 131.03, 129.61, 128.80, 128.77, 128.74, 128.31, 66.07.



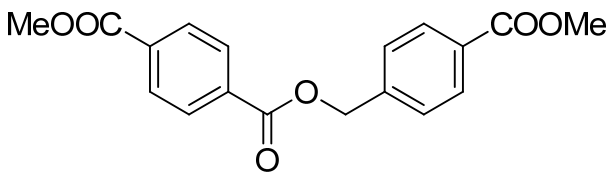
4-(Trifluoromethyl)benzyl 4-(trifluoromethyl)benzoate (3e)[8]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 5.35 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.03, 139.52, 134.97, 134.54, 132.94, 130.86, 130.43, 130.11, 128.25, 125.68, 125.63, 125.58, 125.53, 125.48, 122.15, 121.74, 66.23.



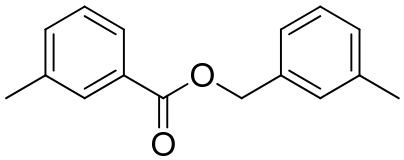
Octyl octanoate (3f)[9]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.98 (t, *J* = 6.7 Hz, 2H), 2.21 (t, *J* = 7.5 Hz, 2H), 1.3 – 1.46 (m, 4H), 1.32 – 1.10 (m, 18H), 0.85 – 0.74 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.93, 64.32, 34.34, 31.83, 31.75, 29.39, 29.24, 29.17, 28.60, 25.90, 24.98, 22.62, 14.04.



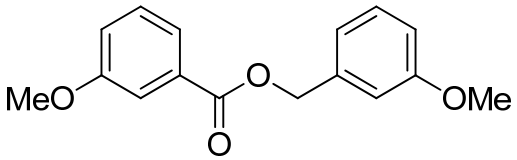
4-Fluorobenzyl 4-fluorobenzoate (3g)[10]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.0, 5.7 Hz, 2H), 7.33 (dd, *J* = 7.9, 5.6 Hz, 2H), 7.10 – 6.85 (m, 4H), 5.22 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.49, 165.35, 164.31, 164.12, 161.03, 132.26, 132.13, 131.73, 131.69, 130.28, 130.17, 126.24, 126.20, 115.67, 115.38, 66.09.



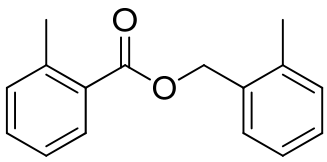
4-(Methoxycarbonyl)benzyl methyl terephthalate (3h)[11]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 4H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 5.34 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.74, 166.25, 165.52, 140.76, 134.25, 133.65, 130.20, 130.04, 129.77, 129.71, 127.87, 66.41, 52.56, 52.28.



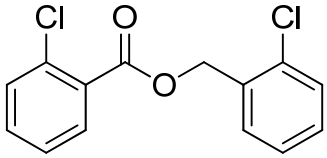
3-Methylbenzyl 3-methylbenzoate (3i)[7]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.95 (d, *J* = 6.5 Hz, 2H), 7.42 – 7.22 (m, 5H), 7.16 (d, *J* = 6.2 Hz, 1H), 5.34 (s, 2H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.57, 138.19, 138.07, 135.97, 133.69, 130.15, 130.04, 128.92, 128.90, 128.43, 128.19, 126.80, 125.23, 66.63, 21.33, 21.19.



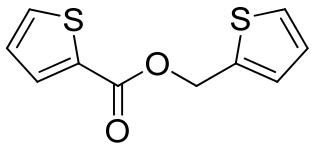
3-Methoxybenzyl 3-methoxybenzoate (3j)[12]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 6.0 Hz, 1H), 7.50 (s, 1H), 7.28 – 7.12 (m, 2H), 7.03 – 6.96 (m, 1H), 6.95 – 6.83 (m, 2H), 6.77 (d, *J* = 7.0 Hz, 1H), 5.23 (s, 2H), 3.71 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.15, 159.67, 159.46, 137.46, 131.30, 129.56, 129.31, 121.99, 120.19, 119.38, 114.12, 113.54, 66.50, 55.30, 55.11.



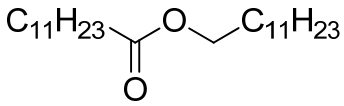
2-Methylbenzyl 2-methylbenzoate (3k)[13]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 6.7 Hz, 1H), 7.43 – 7.08 (m, 5H), 5.26 (s, 2H), 2.51 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.24, 140.35, 136.91, 134.03, 131.98, 131.67, 130.61, 130.33, 129.38, 129.22, 128.43, 125.99, 125.66, 64.85, 21.75, 18.95.



2-Chlorobenzyl 2-chlorobenzoate (3l)[13]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.41 (m, 1H), 7.41 – 7.29 (m, 3H), 7.27 – 7.16 (m, 3H), 5.40 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.18, 133.80, 133.24, 132.70, 131.58, 131.10, 130.56, 130.14, 129.65, 129.59, 128.38, 126.90, 126.58, 64.62.



Thiophen-2-ylmethyl thiophene-2-carboxylate (3m)[9]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 2.7 Hz, 1H), 7.47 (d, *J* = 4.5 Hz, 1H), 7.26 (d, *J* = 4.8 Hz, 1H), 7.06-7.12 (m, 1H), 7.01 (d, *J* = 4.2 Hz, 1H), 6.92 (d, *J* = 4.2 Hz, 1H), 5.40 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.85, 137.68, 133.77, 132.68, 129.60, 128.37, 127.74, 126.96, 126.80, 61.01.



Dodecyl dodecanoate (3n)[14]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.98 (t, *J* = 6.7 Hz, 2H), 2.21 (t, *J* = 7.5 Hz, 2H), 1.80 – 1.51 (m, 4H), 1.10-1.35 (m, 34H), 0.75-0.87 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.27, 64.64, 63.26, 34.65, 33.08, 32.19, 29.90, 29.81, 29.75, 29.63, 29.55, 29.43, 28.91, 26.20, 26.03, 25.29, 22.95, 14.38.

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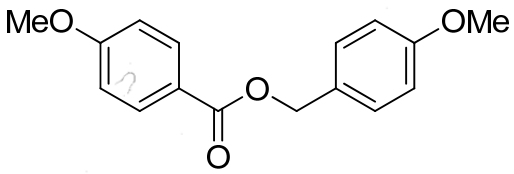
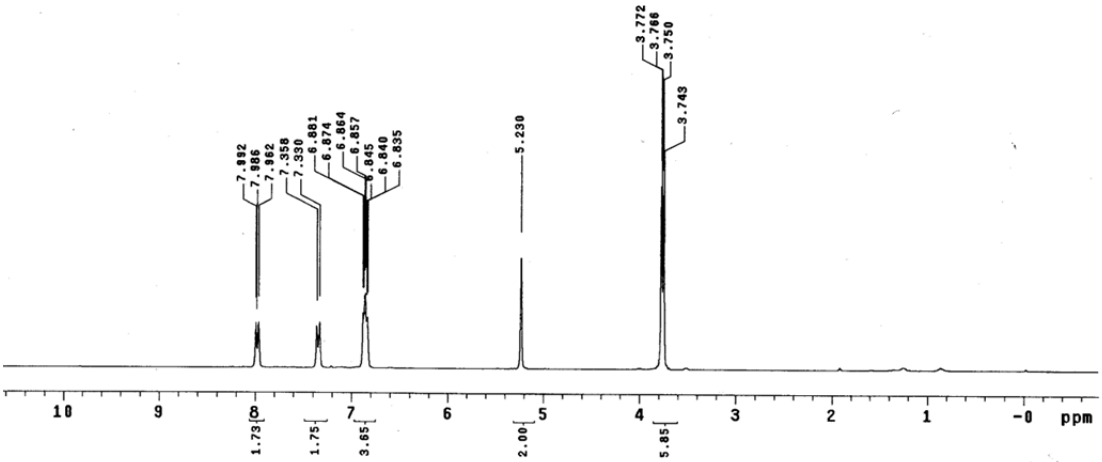
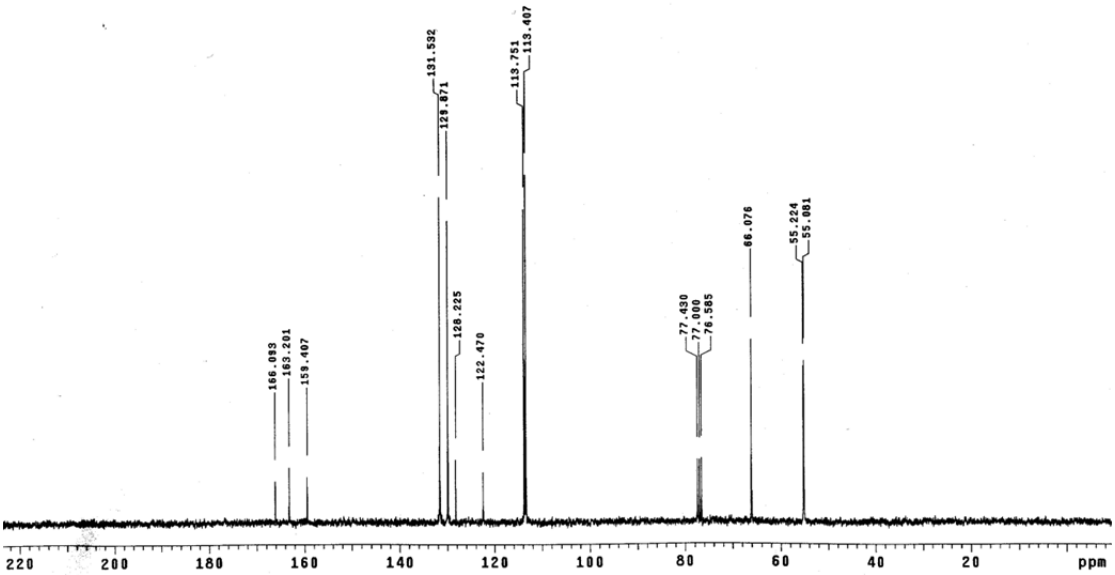
Copies of product ^{1}H NMR and ^{13}C NMR

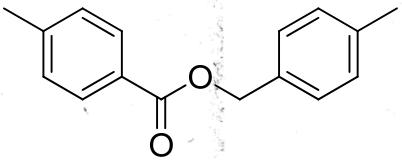
3a

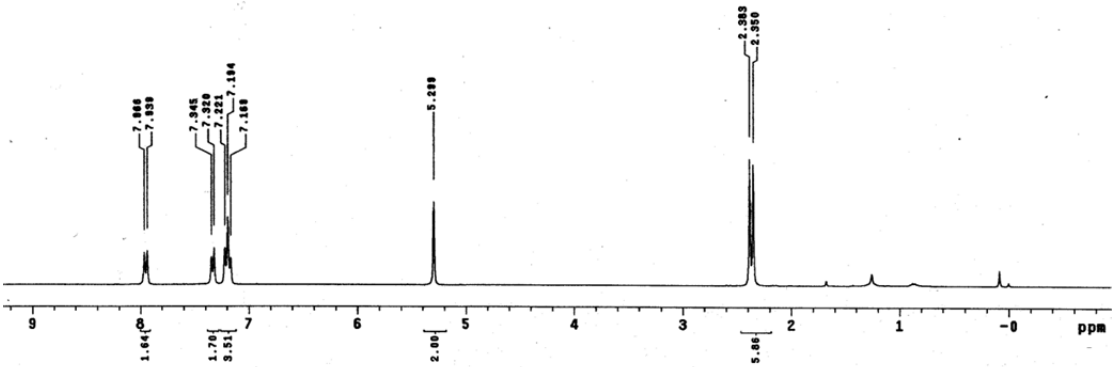


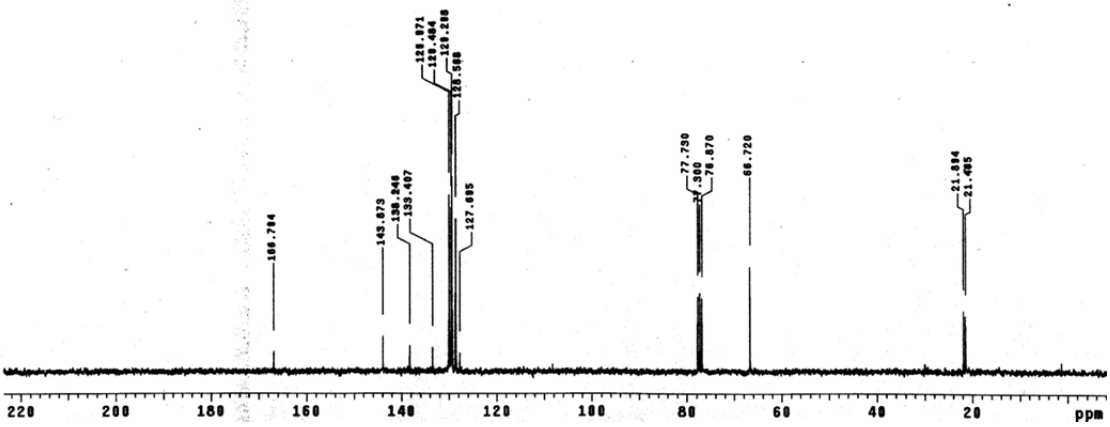




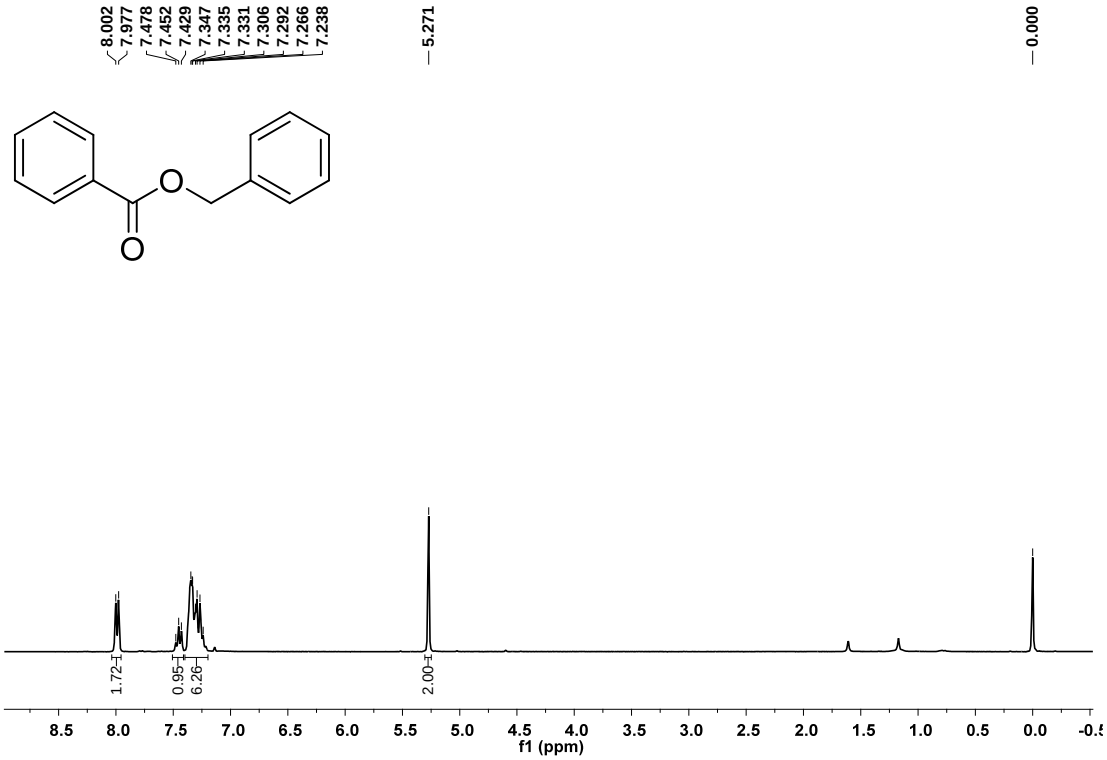
3b

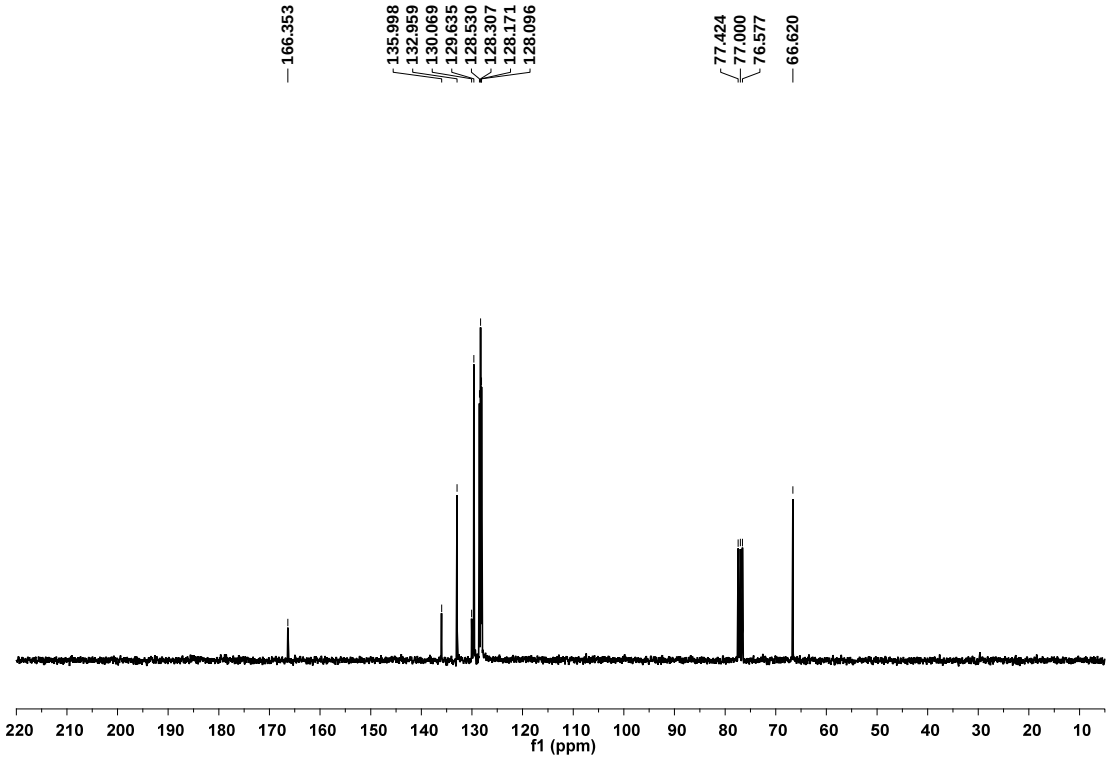




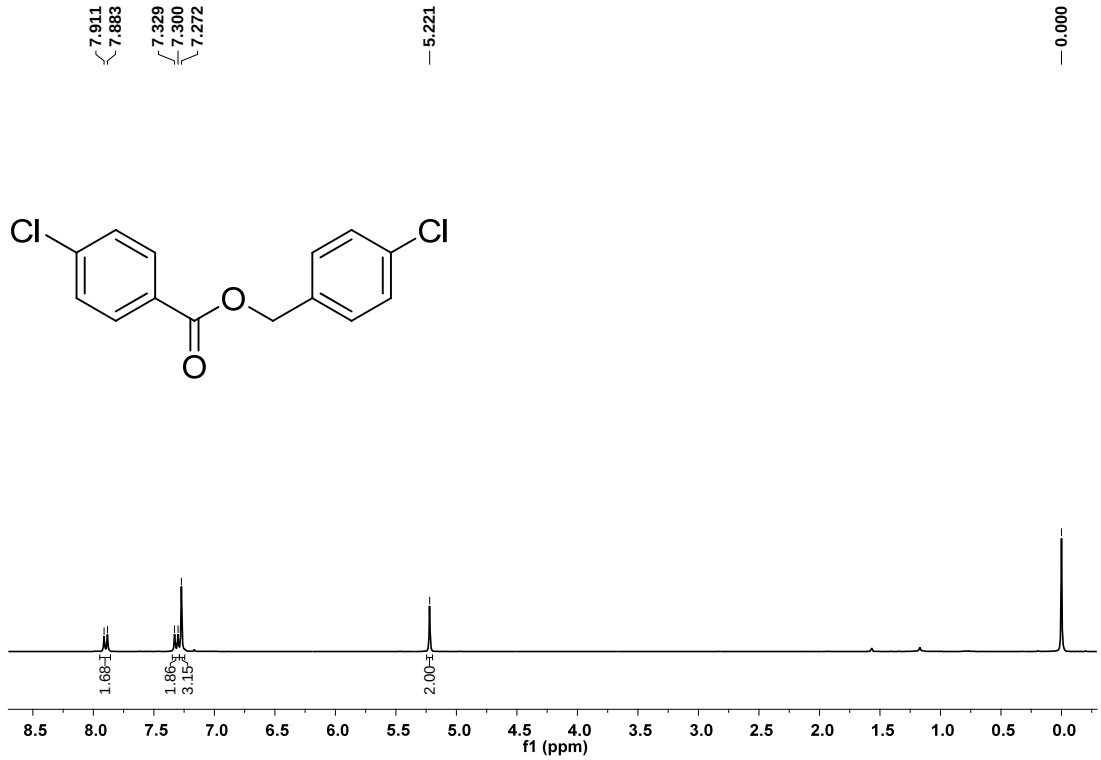


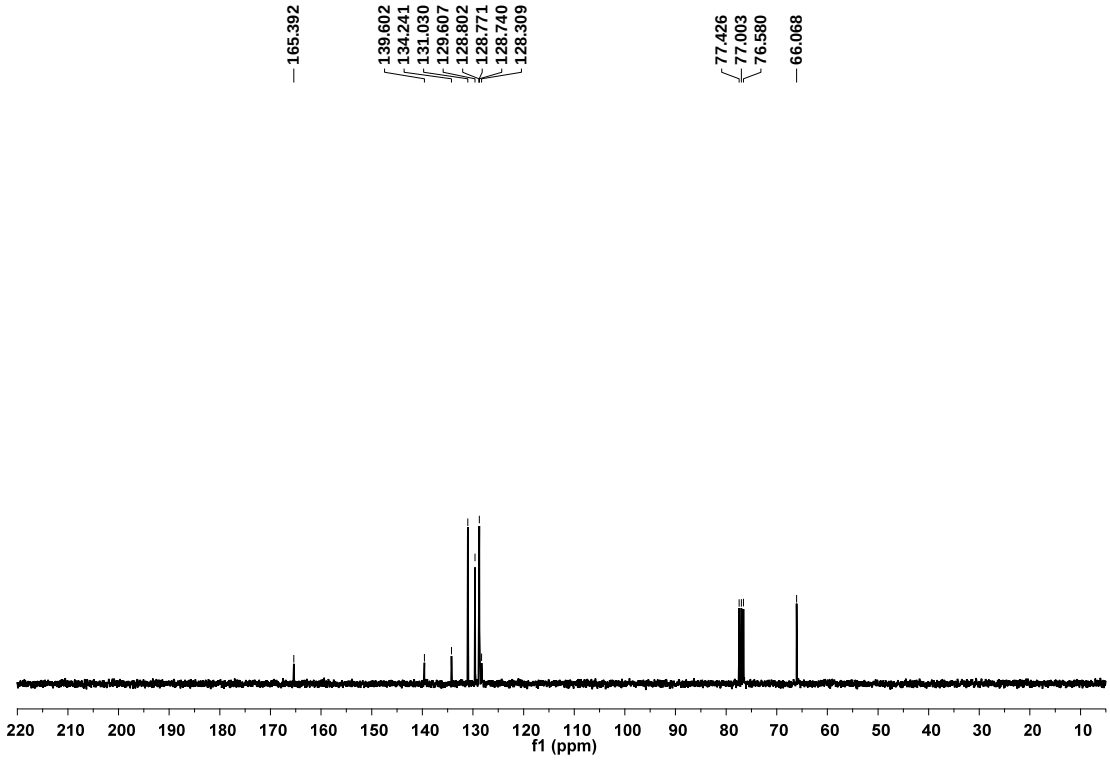
3c


8.002
7.977
7.478
7.452
7.429
7.347
7.335
7.331
7.306
7.292
7.266
7.238
5.271
0.000
1.72
0.95
6.26
2.00
f1 (ppm)

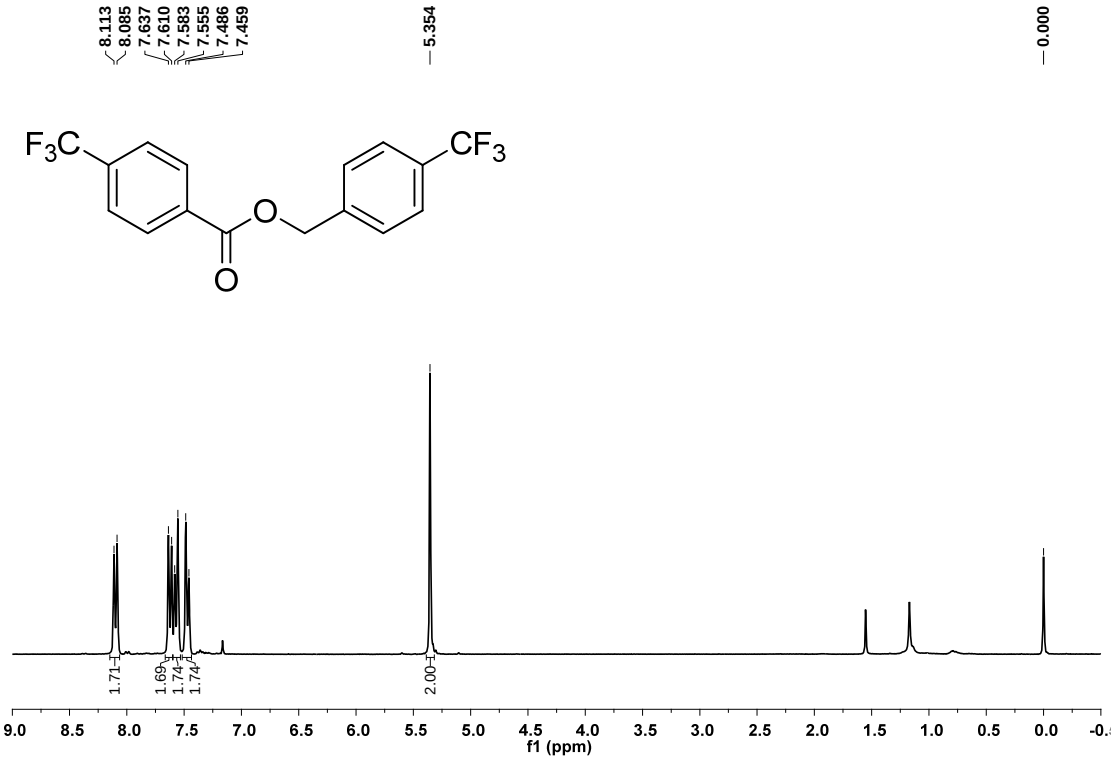

166.353
135.998
132.959
130.069
129.635
128.530
128.307
128.171
128.096
77.424
77.000
76.577
66.620
f1 (ppm)

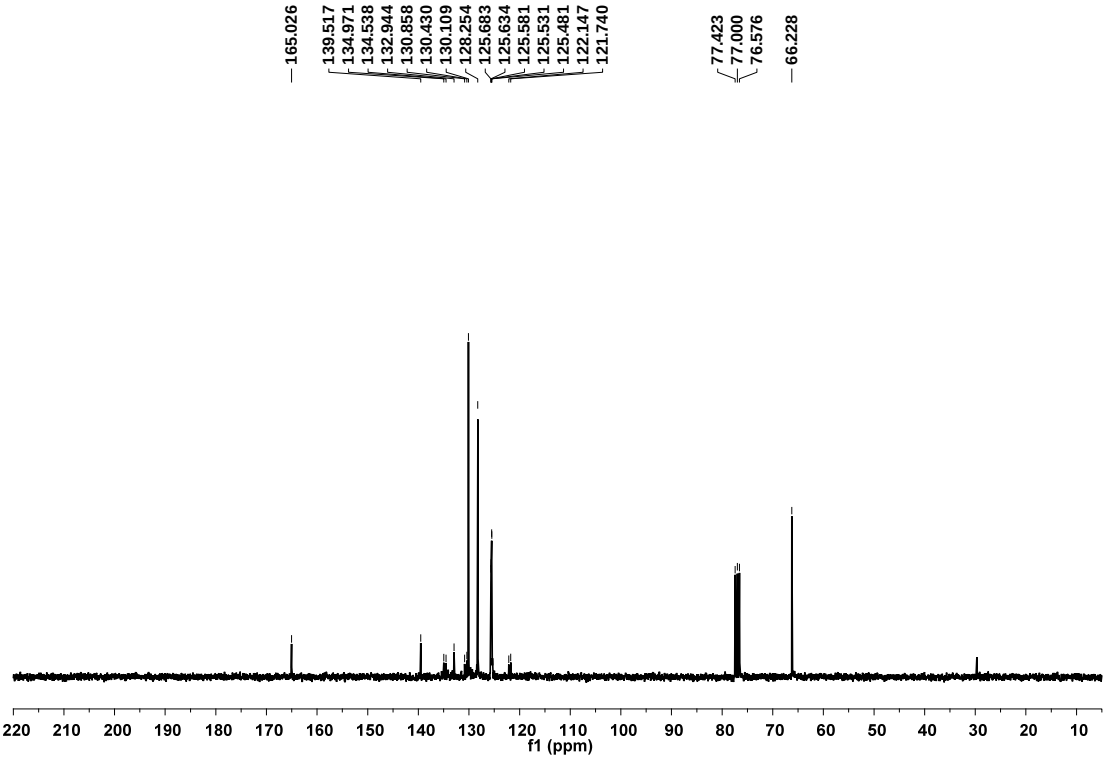
3d


7.911
7.883
7.329
7.300
7.272
5.221
0.000
Cl
Cl
O
O
1.68
1.86
3.15
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

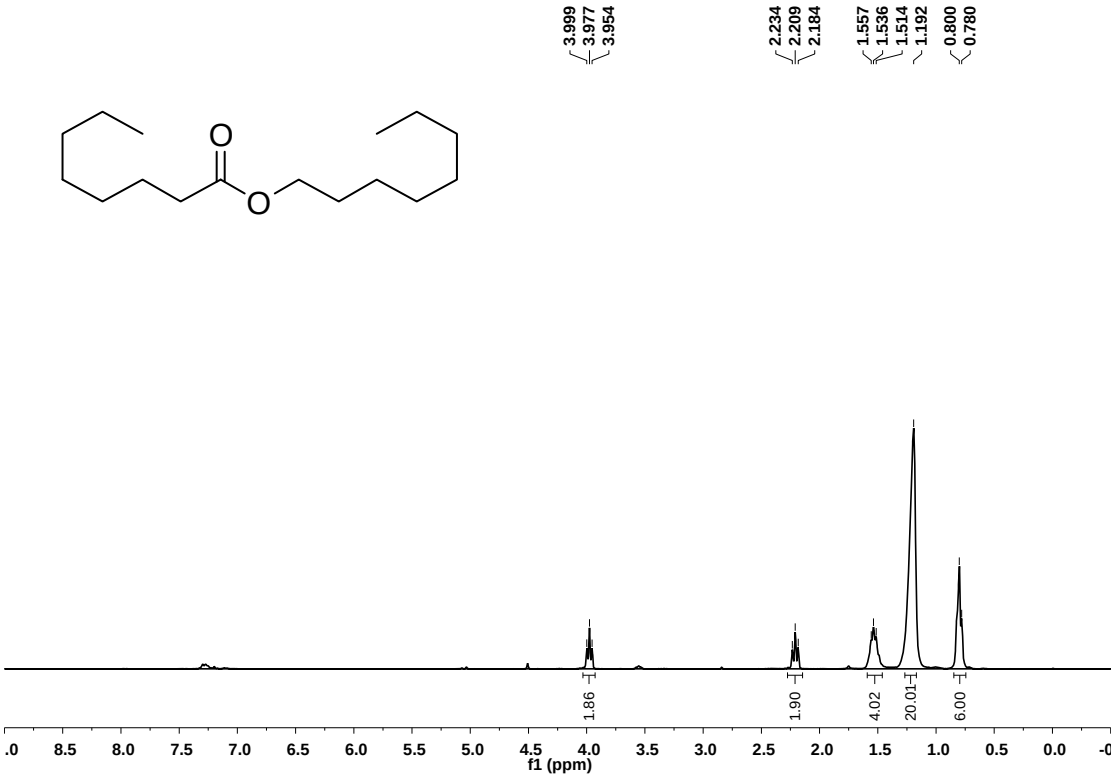

165.392
139.602
134.241
131.030
129.607
128.802
128.771
128.740
128.309
77.426
77.003
76.580
66.068
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

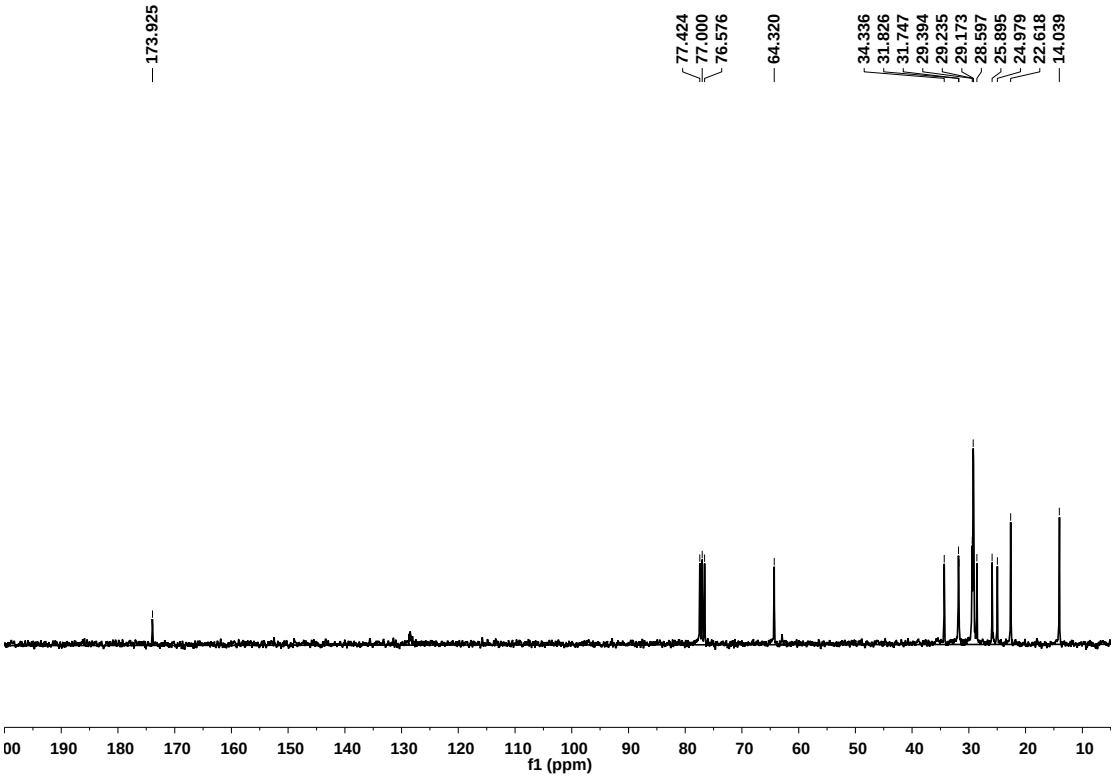
3e


8.113
8.085
7.637
7.610
7.583
7.555
7.486
7.459
5.354
0.000
F3C
CF3
O
O
1.71
1.69
1.74
1.74
2.00
f1 (ppm)

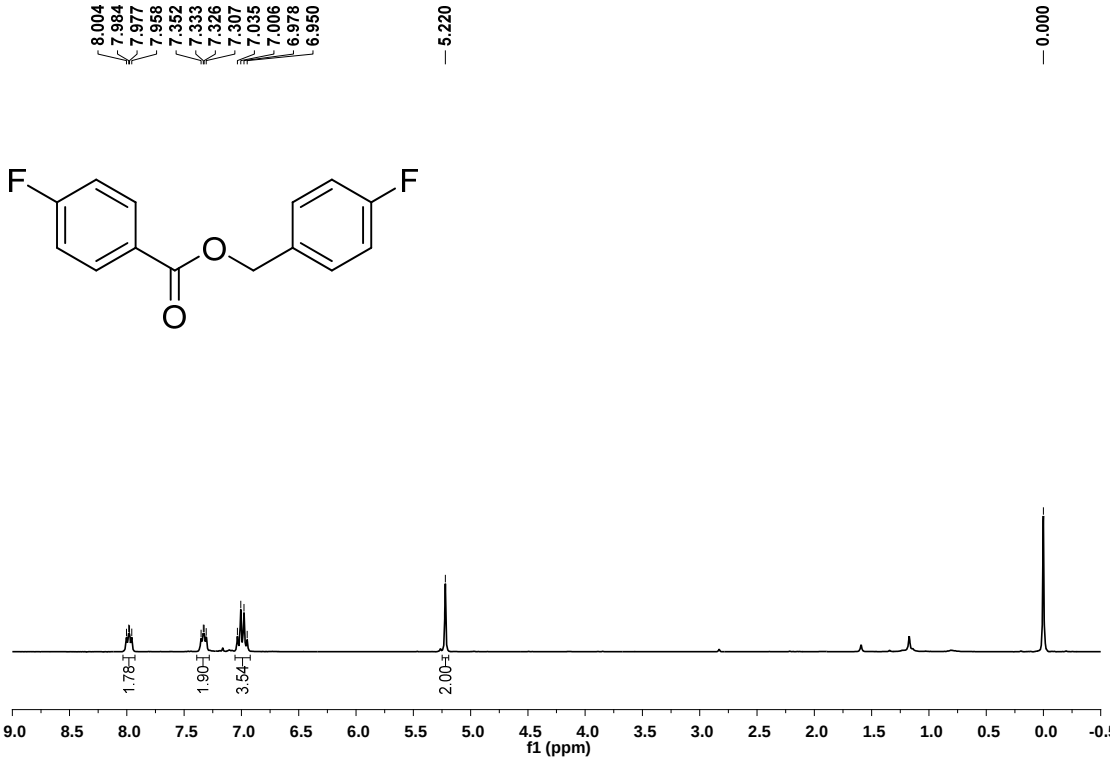

165.026
139.517
134.971
134.538
132.944
130.858
130.430
130.109
128.254
125.683
125.634
125.581
125.531
125.481
122.147
121.740
77.423
77.000
76.576
66.228
f1 (ppm)

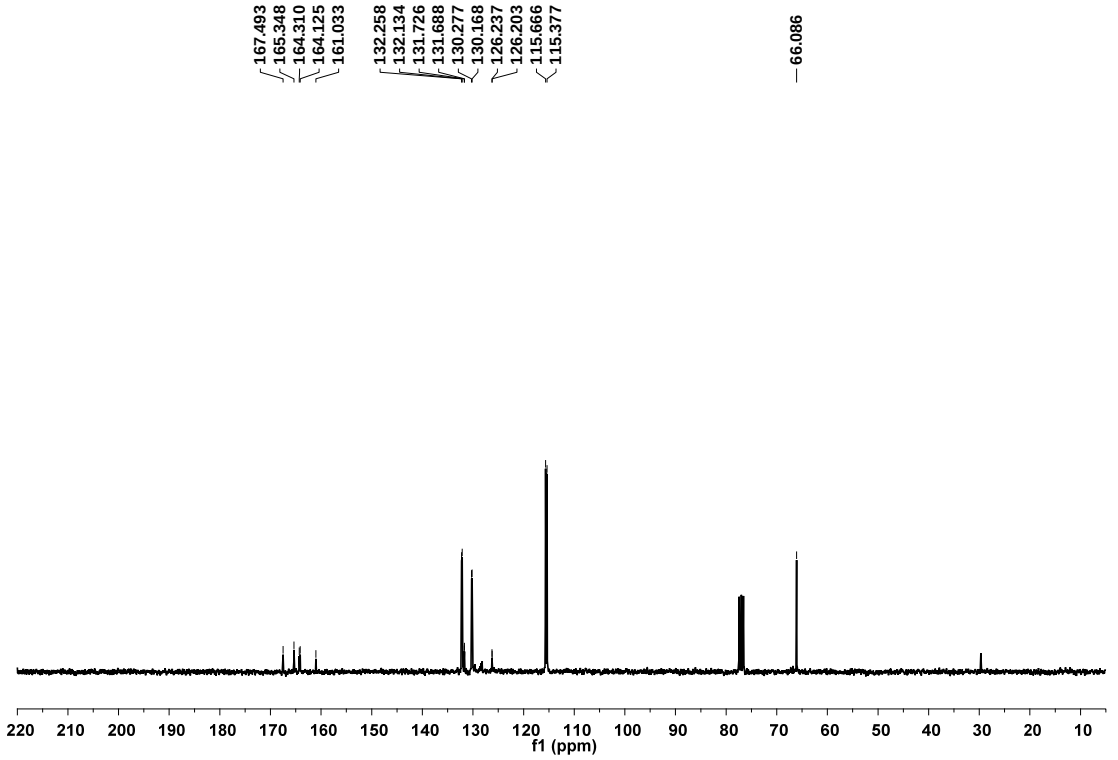
3f


3.999
3.977
3.954
2.234
2.209
2.184
1.557
1.536
1.514
1.192
0.800
0.780
1.86
1.90
4.02
20.01
6.00
f1 (ppm)

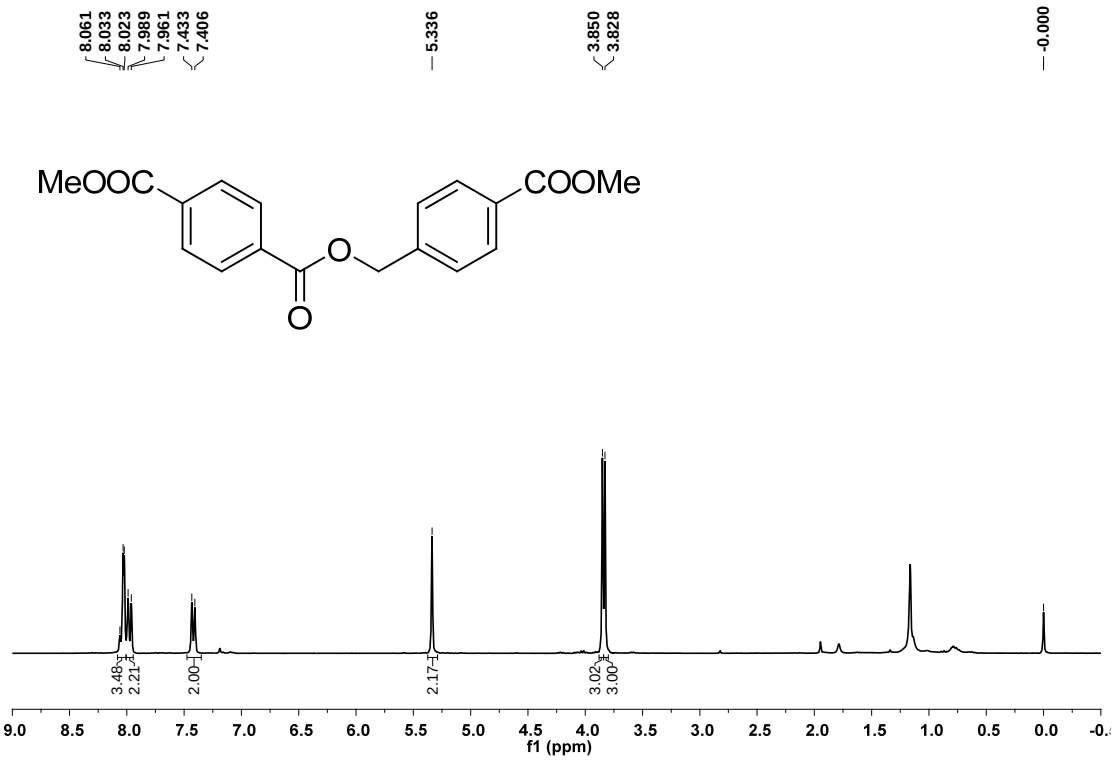

173.925
77.424
77.000
76.576
64.320
34.336
31.826
31.747
29.394
29.235
29.173
28.597
25.895
24.979
22.618
14.039
f1 (ppm)

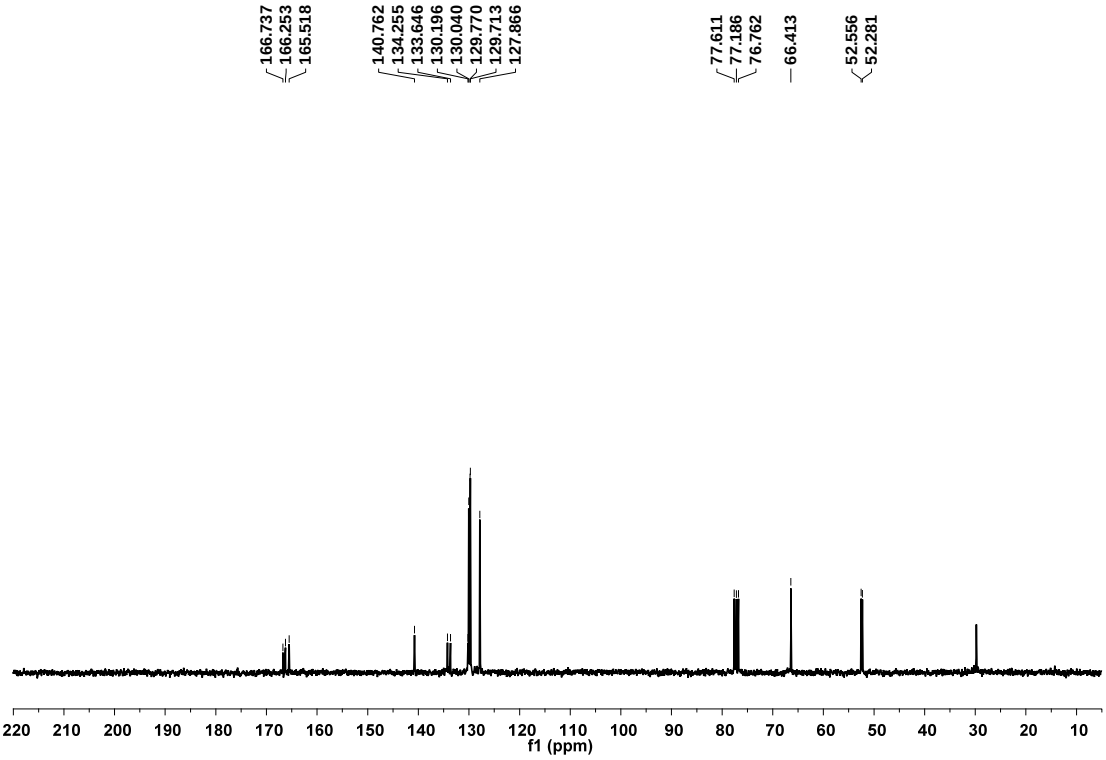
3g


8.004
7.984
7.977
7.958
7.352
7.333
7.326
7.307
7.035
7.006
6.978
6.950
5.220
0.000
F
F
O
O
1.78
1.90
3.54
2.00
f1 (ppm)

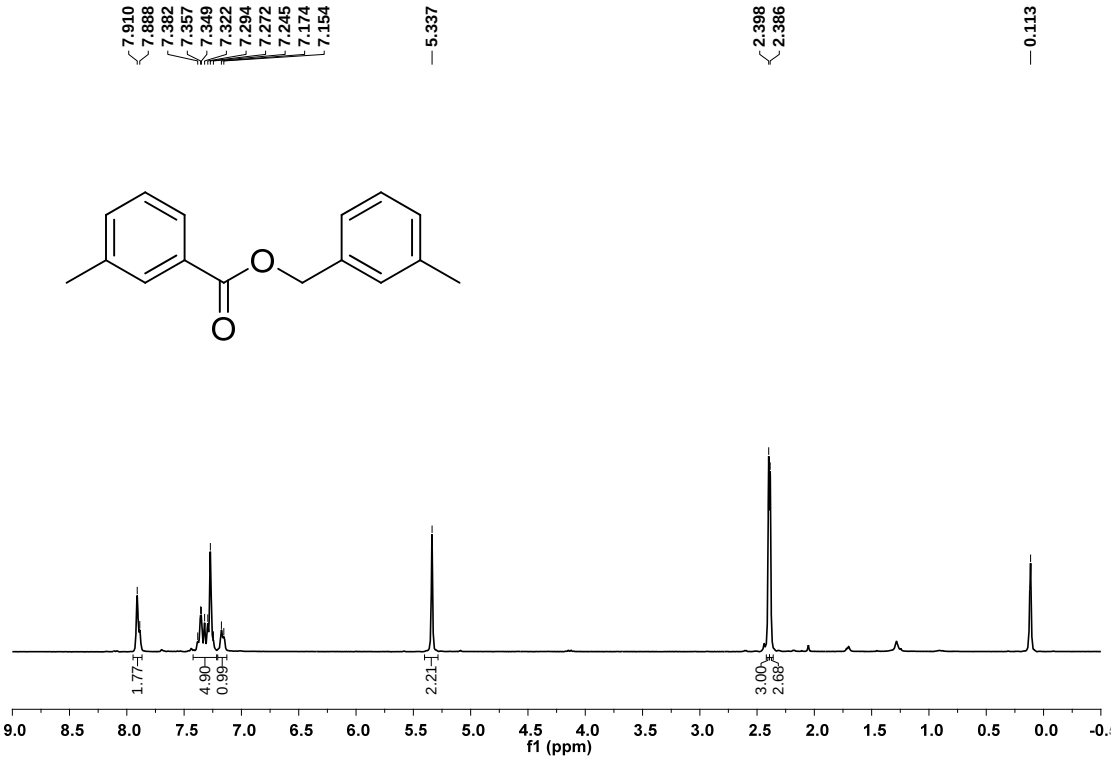

167.493
165.348
164.310
164.125
161.033
132.258
132.134
131.726
131.688
130.277
130.168
126.237
126.203
115.666
115.377
66.086
f1 (ppm)

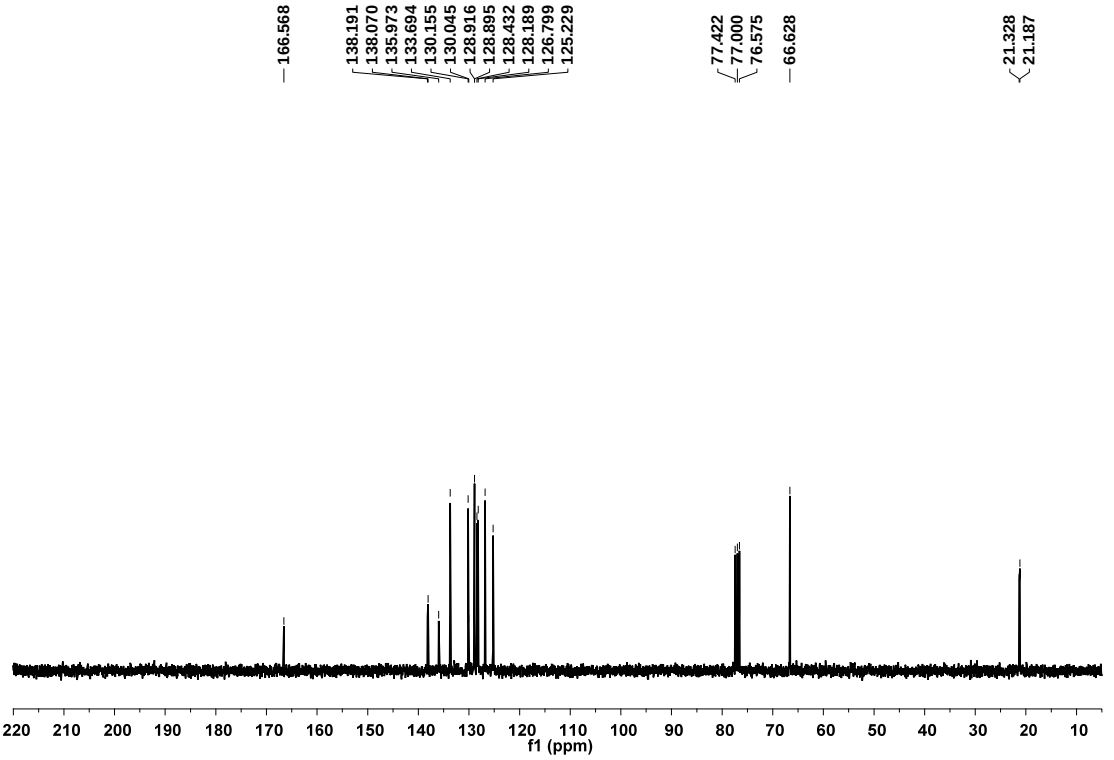
3h


8.061
8.033
8.023
7.989
7.961
7.433
7.406
5.336
3.850
3.828
-0.000
MeOOC
COOMe
O
O
3.48
2.21
2.00
2.17
3.02
3.00
f1 (ppm)

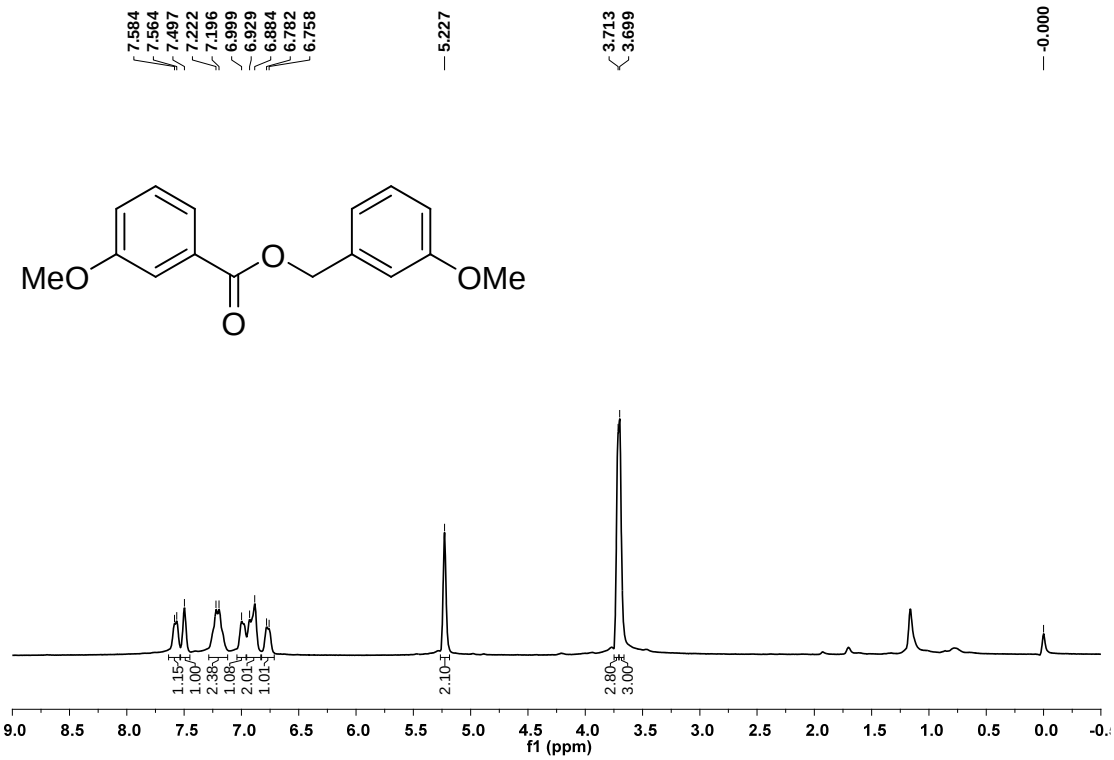

166.737
166.253
165.518
140.762
134.255
133.646
130.196
130.040
129.770
129.713
127.866
77.611
77.186
76.762
66.413
52.556
52.281
f1 (ppm)

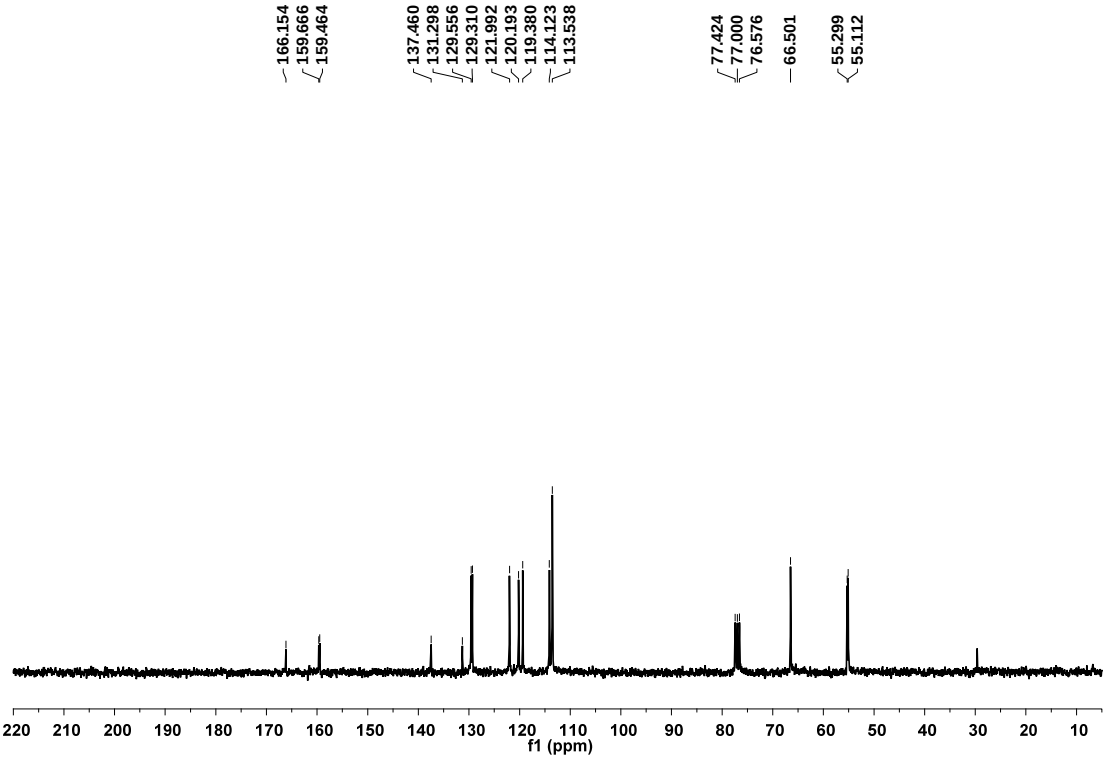
3i


7.910
7.888
7.382
7.357
7.349
7.322
7.294
7.272
7.245
7.174
7.154
5.337
2.398
2.386
0.113
1.77
4.90
0.99
2.21
3.00
2.68
f1 (ppm)

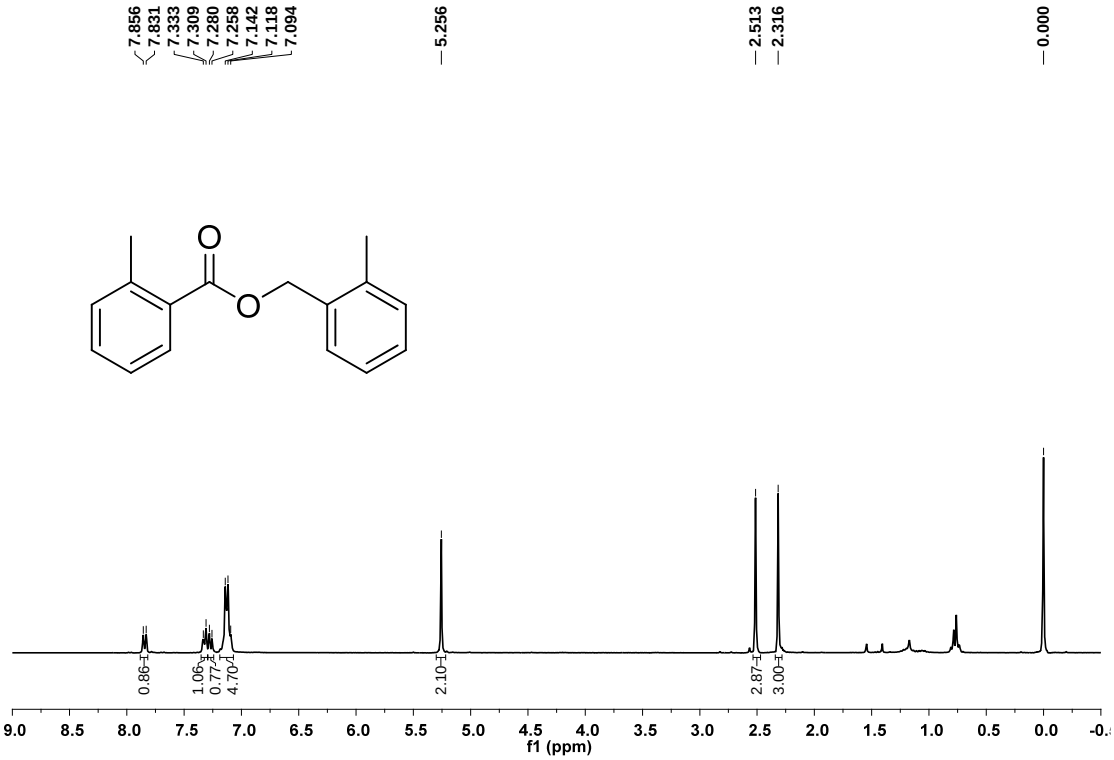

166.568
138.191
138.070
135.973
133.694
130.155
130.045
128.916
128.895
128.432
128.189
126.799
125.229
77.422
77.000
76.575
66.628
21.328
21.187
f1 (ppm)

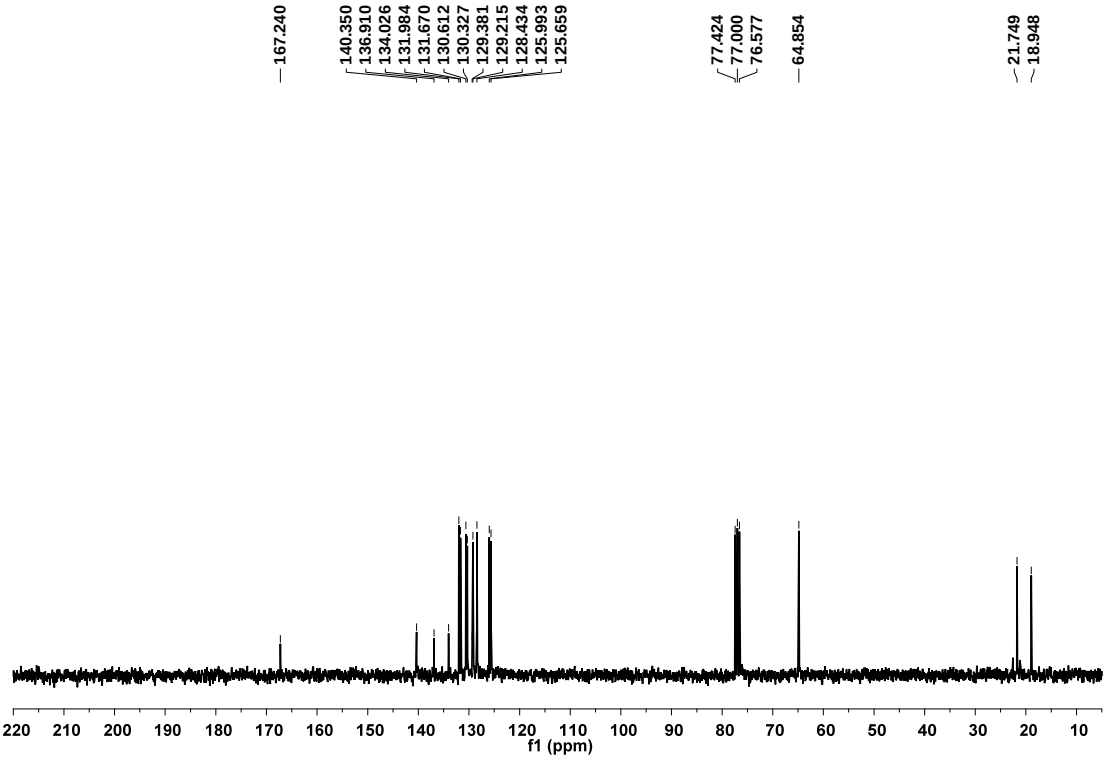
3j


7.584
7.564
7.497
7.222
7.196
6.999
6.929
6.884
6.782
6.758
5.227
3.713
3.699
-0.000
MeO
O
O
OMe
1.15
1.00
2.38
1.08
2.01
1.01
2.10
2.80
3.00
f1 (ppm)

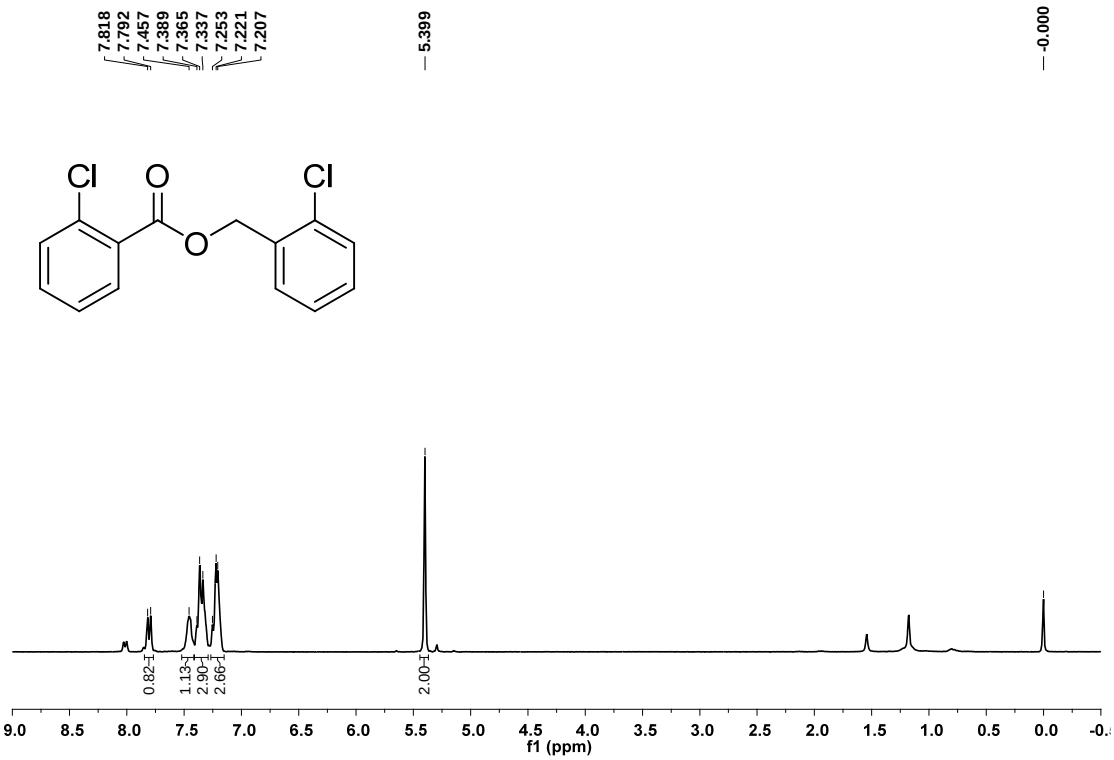

166.154
159.666
159.464
137.460
131.298
129.556
129.310
121.992
120.193
119.380
114.123
113.538
77.424
77.000
76.576
66.501
55.299
55.112
f1 (ppm)

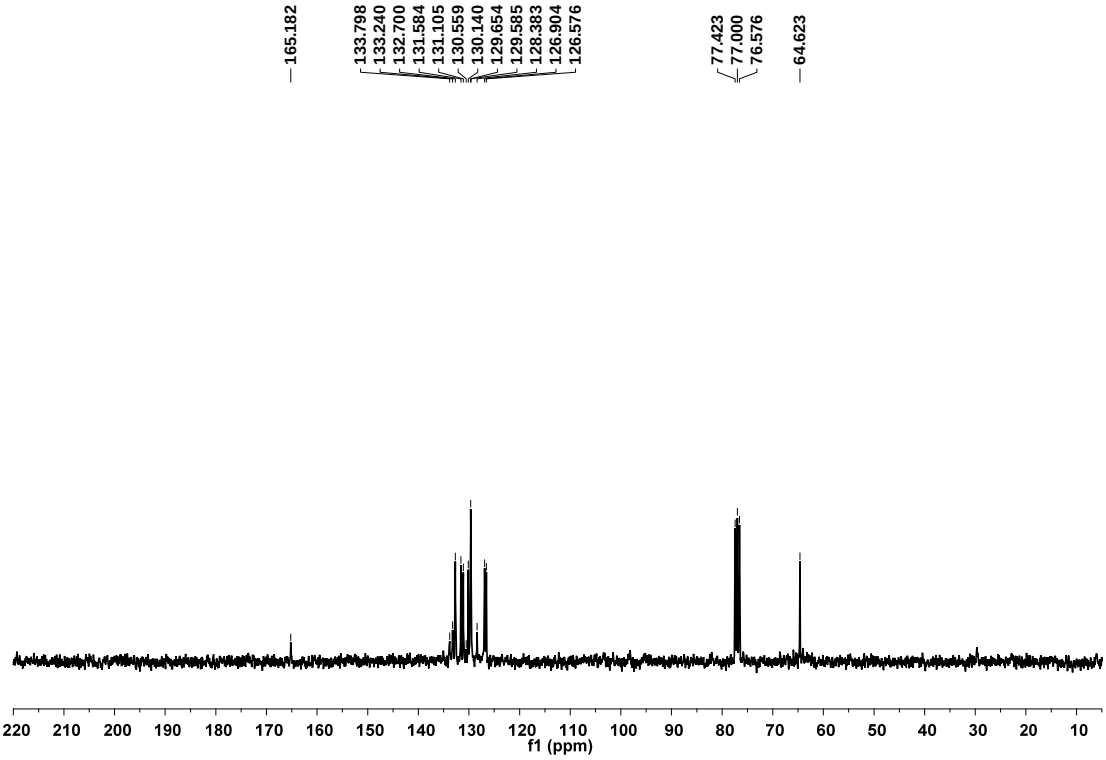
3k


7.856
7.831
7.333
7.309
7.280
7.258
7.142
7.118
7.094
5.256
2.513
2.316
0.000
O
O
0.86
1.06
0.77
4.70
2.10
2.87
3.00
f1 (ppm)

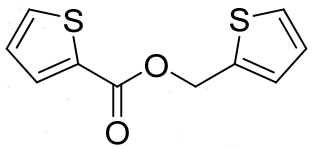

167.240
140.350
136.910
134.026
131.984
131.670
130.612
130.327
129.381
129.215
128.434
125.993
125.659
77.424
77.000
76.577
64.854
21.749
18.948
f1 (ppm)

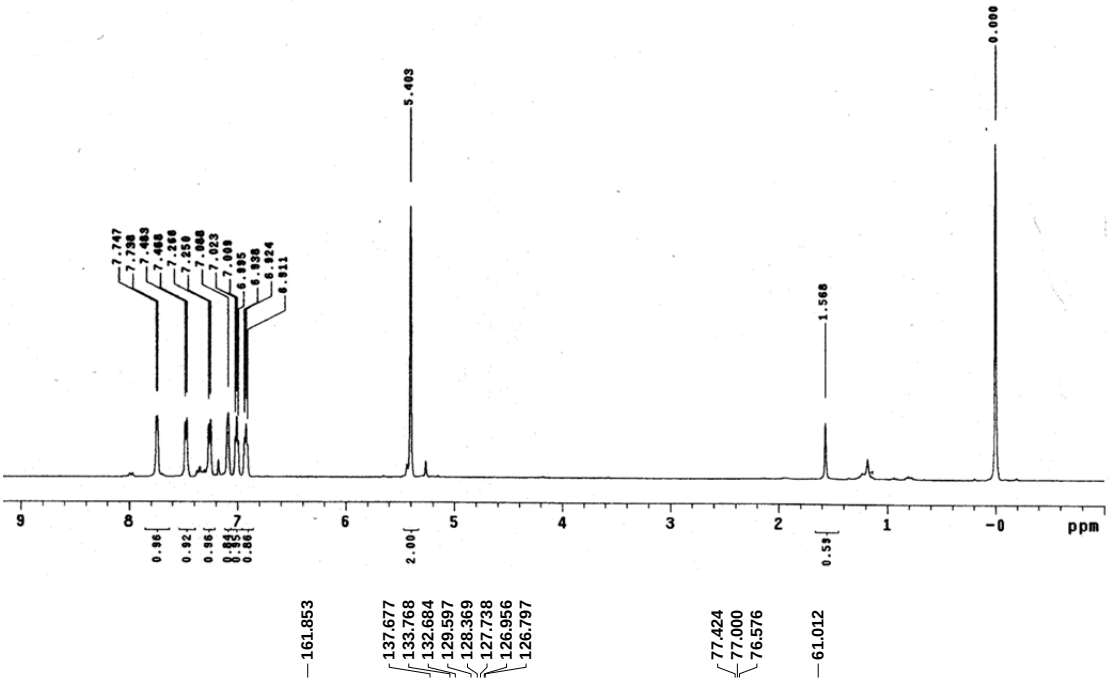
3l

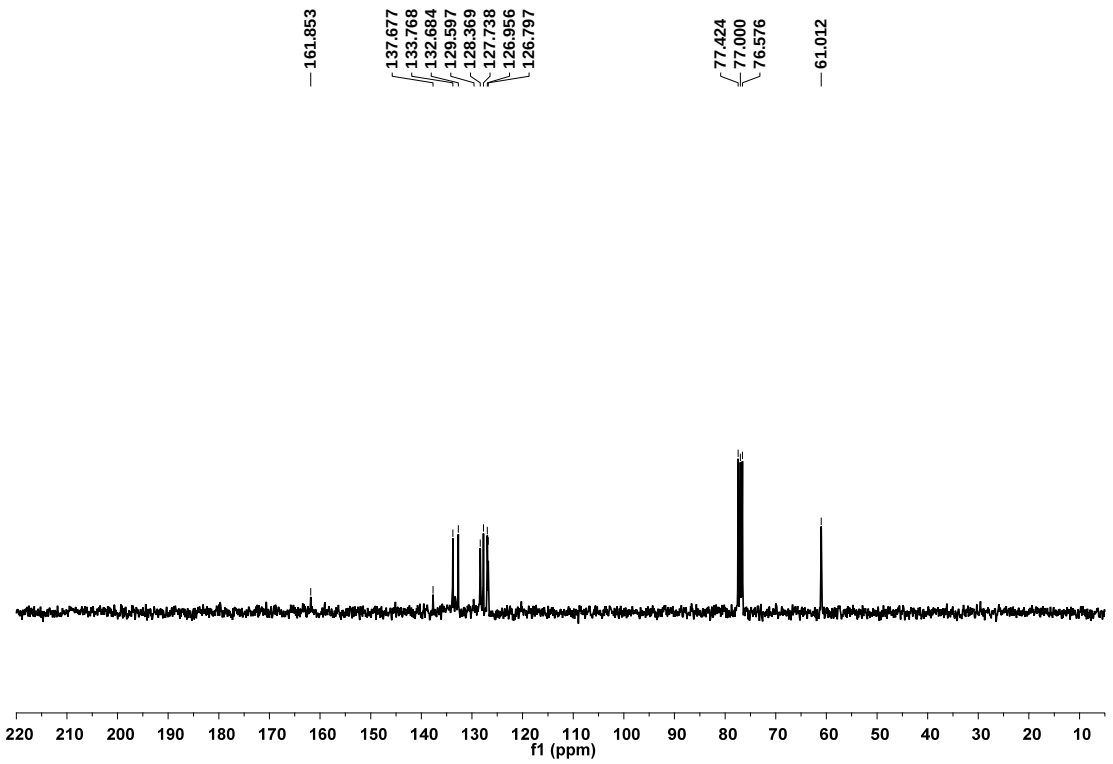

7.818
7.792
7.457
7.389
7.365
7.337
7.253
7.221
7.207
5.399
-0.000
Cl
O
Cl
O
0.82
1.13
2.90
2.66
2.00
f1 (ppm)


165.182
133.798
133.240
132.700
131.584
131.105
130.559
130.140
129.654
129.585
128.383
126.904
126.576
77.423
77.000
76.576
64.623
f1 (ppm)

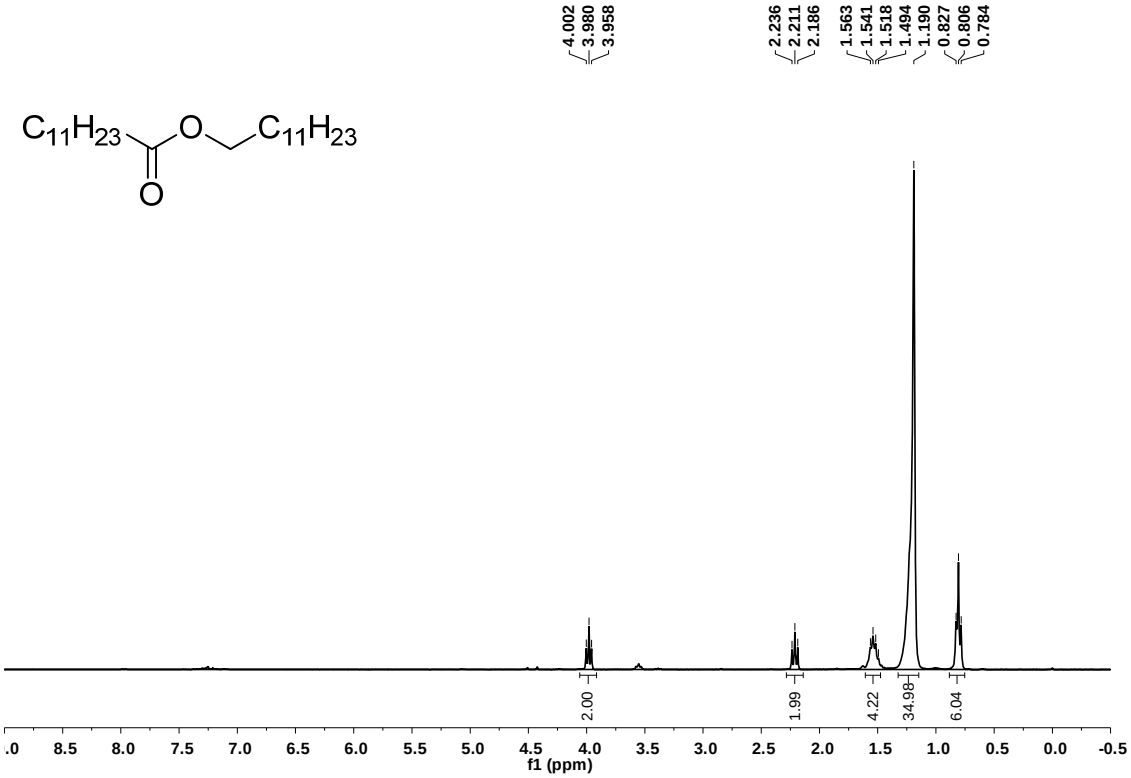
3m

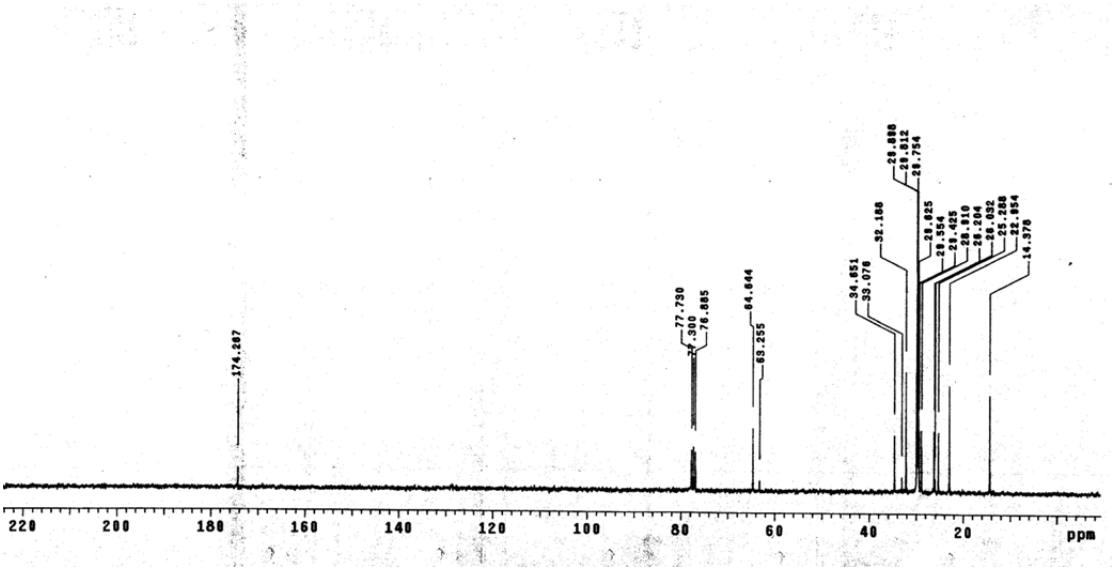



7.747
7.738
7.483
7.468
7.266
7.250
7.068
7.023
7.009
6.995
6.938
6.924
6.911
5.403
1.568
0.000
9
8
7
6
5
4
3
2
1
-0
ppm
0.96
0.92
0.96
0.84
0.95
0.86
2.00
0.59


161.853
137.677
133.768
132.684
129.597
128.369
127.738
126.956
126.797
77.424
77.000
76.576
61.012
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3n


4.002
3.980
3.958
2.236
2.211
2.186
1.563
1.541
1.518
1.494
1.190
0.827
0.806
0.784
C11H23
O
C11H23
O
2.00
1.99
4.22
34.98
6.04
f1 (ppm)


174.287
77.730
77.300
76.885
64.644
63.255
34.651
33.076
32.188
28.808
28.812
28.754
28.625
28.554
28.425
28.010
26.204
26.032
25.288
22.854
14.378
ppm